

DECLARATION

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do hereby solemnly and sincerely declare:-

- 1) THAT I am well acquainted with the Japanese language
and English language, and
- 2) THAT the attached is a full, true, accurate and
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The undersigned declares further that all
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Signed this 22nd day of March , 2004 .


Itsuko KAJIWARA



ATTACHMENT - Translation
of Japanese priority document

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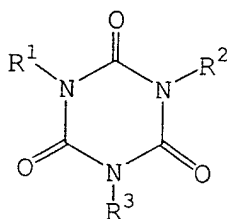
[Title of Document] Specification

[Title of the Invention] NON-AQUEOUS ELECTROLYTE
BATTERY AND NON-AQUEOUS
ELECTROLYTE

[Scope of Claim for a Patent]

[Claim 1] A non-aqueous electrolyte battery
containing a positive electrode, a negative electrode
5 and a non-aqueous electrolyte comprising an electrolyte
salt dissolved in an organic solvent, wherein the non-
aqueous electrolyte contains a compound represented by
the following formula:

[Formula 1]



(in the above formula, R¹, R² and R³ independently
10 represent a hydrogen atom, a halogen atom or a straight
chain or branched chain alkyl group).

[Claim 2] A non-aqueous electrolyte battery
according to claim 1, wherein said compound is at least
one compound selected from the group consisting of
15 tris(2-carboxyethyl) isocyanurate and derivatives
thereof.

[Claim 3] A non-aqueous electrolyte battery

according to claim 1, wherein said compound is tris(2-methoxycarboxyethyl) isocyanurate.

[Claim 4] A non-aqueous electrolyte battery according to claim 1, wherein said organic solvent is at least one organic compound selected from the group consisting of carbonic acid esters, cyclic carboxylic acid esters and phosphoric acid esters.

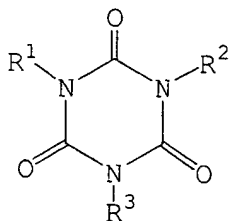
[Claim 5] A non-aqueous electrolyte battery according to claim 1, wherein the content of the compound is not less than 0.01% by weight and less than 20% by weight based on the weight of the non-aqueous electrolyte.

[Claim 6] A non-aqueous electrolyte battery according to claim 1, wherein the negative electrode comprises a carbon material.

[Claim 7] A non-aqueous electrolyte battery according to claim 6, wherein the carbon material is a material obtained by graphitizing mesophase spherule at a high temperature.

[Claim 8] A non-aqueous electrolyte containing an organic solvent and an electrolyte salt, wherein the non-aqueous electrolyte contains a compound represented by the following formula:

[Formula 2]



in the above formula, R¹, R² and R³ independently represent a hydrogen atom, a halogen atom or a straight chain or branched chain alkyl group.

[Claim 9] A non-aqueous electrolyte according to
5 claim 8, wherein said compound is at least one compound selected from the group consisting of tris(2-carboxyethyl) isocyanurate and derivatives thereof.

[Claim 10] A non-aqueous electrolyte according to
claim 8, wherein said compound is tris(2-
10 methoxycarboxyethyl) isocyanurate.

[Claim 11] A non-aqueous electrolyte according to
claim 8, wherein said organic solvent is at least one organic compound selected from the group consisting of carbonic acid esters, cyclic carboxylic acid esters and
15 phosphoric acid esters.

[Claim 12] A non-aqueous electrolyte according to
claim 8, wherein the content of the compound is 20% by weight based on the weight of the non-aqueous electrolyte.

20 [Detailed Description of the Invention]

[0001]

[Technical Field Pertinent to the Invention]

The present invention relates to a non-aqueous electrolyte battery, and, particularly, to an
25 improvement of a non-aqueous electrolyte.

[0002]

[Prior Art]

At present, as organic solvents which constitute non-aqueous electrolytes for non-aqueous electrolyte batteries, there are used, for example, ethylene carbonate, propylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, ethylmethyl carbonate, dipropyl carbonate, methyl propionate, tetrahydrofuran, 1,3-dioxolan, and 1,2-dimethoxyethane each alone or in admixture. As electrolyte salts, there are used, for example, LiClO_4 , LiBF_4 , LiPF_6 , LiCF_3SO_3 , and $(\text{CF}_3\text{SO}_2)_2\text{NLi}$ each alone or in admixture. Especially, carbonic acid esters are mainly used as organic solvents and LiPF_6 is mainly used as electrolyte salts because they are superior in conductivity and are safe for environments.

[0003]

[Problems to be solved by the Invention]

However, when batteries made using non-aqueous electrolytes comprising the above organic solvents and electrolyte salts are stored in charged state, electrode materials react with the organic solvents and the electrolyte salts to cause decomposition of the non-aqueous electrolytes, and, as a result, capacity of the batteries after stored tends to decrease. Especially, in secondary batteries which are made using carbon materials as negative electrode materials, occurrence of reduction reaction at negative electrodes is accelerated and said tendency becomes more conspicuous.

[0004]

The object of the present invention is to provide a non-aqueous electrolyte battery which is inhibited from the deterioration of non-aqueous electrolyte when stored in charged state, especially, the occurrence of reaction between the negative electrode materials and the non-aqueous electrolyte and, thus, which has excellent storage characteristics.

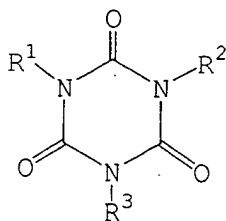
[0005]

10 [Means for Solving Problem]

For attaining the above object, the present invention provides a non-aqueous electrolyte battery having a positive electrode, a negative electrode and a non-aqueous electrolyte prepared by dissolving an electrolyte salt in an organic solvent, wherein the non-aqueous electrolyte contains a compound represented by the following formula:

[0006]

[Formula 3]



20 [0007]

(in the above formula, R¹, R² and R³ independently represent a hydrogen atom, a halogen atom or a straight chain or branched chain alkyl group, and the alkyl group

may contain a hydroxyl group, carboxyl group, aldehyde group, carbonyl group, ether linkage or ester linkage). This compound when added to the electrolyte forms a film on the surface of the negative electrode to prevent the electrolyte and the negative electrode from contacting with each other. As a result, occurrence of decomposition reaction of the electrolyte on the negative electrode can be diminished.

[0008]

10 A preferred embodiment of the present invention is that the compound is represented by the formula (3) where R^1 , R^2 and R^3 independently of one another are each an alkyl group having a carboxyl group or an alkyl group containing an ester linkage. A more preferred embodiment is that the compound represented by the formula (3) is at least one of tris(2-carboxyethyl) isocyanurate and a derivative thereof, (preferably tris(2-methoxycarboxyethyl) isocyanurate). This is because when one of the compounds represented by the formula (3) forms a film on the negative electrode, if the organic compound has a carboxyl group, it positively reacts with active sites on the negative electrode and, hence, reactivity of the active sites on the negative electrode lowers to make it possible to further inhibit the decomposition of the electrolyte on the negative electrode. In the case of having an ester linkage, the same effect can also be obtained by carboxyl group or hydroxyl group produced upon decomposition of the ester

linkage.

[0009]

[Mode for Carrying Out the Invention]

The non-aqueous electrolyte of the present
5 invention contains an organic solvent and an electrolyte
salt which is soluble in the solvent. As the organic
solvent, mention may be made of non-protonic organic
solvents, for example, cyclic carbonic acid esters such
as ethylene carbonate (EC), propylene carbonate (PC) and
10 butylene carbonate (BC), non-cyclic carbonic acid esters
such as dimethyl carbonate (DMC), diethyl carbonate
(DEC), ethylmethyl carbonate (EMC) and dipropyl
carbonate (DPC), aliphatic carboxylic acid esters such
as methyl formate, methyl acetate, methyl propionate and
15 ethyl propionate, cyclic carboxylic acid esters such as
 γ -butyrolactone and γ -valerolactone, non-cyclic ethers
such as 1,2-dimethoxyethane (DME), 1,2-diethoxyethane
(DEE) and ethoxymethoxyethane (EME), cyclic ethers such
as tetrahydrofuran and 2-methyltetrahydrofuran, dimethyl
20 sulfoxide, 1,3-dioxolan, formamide, acetamide,
dimethylformamide, dioxolan, acetonitrile,
propylnitrile, nitromethane, ethyl monoglyme, phosphoric
acid esters such as trimethyl phosphate and thimethyl
phosphate, trimethoxymethane, dioxolan derivatives,
25 sulfolane, methylsulfolane, 1,3-dimethyl-2-
imidazolidinone, 3-methyl-2-oxazolidinone, propylene
carbonate derivatives, tetrahydrofuran derivatives,
ethyl ether, 1,3-propanesultone, anisole, dimethyl

sulfoxide and N-methylpyrrolidone. These are used each alone or in admixture of two or more. Preferably, at least one organic compound selected from the group consisting of the carbonic acid esters, the cyclic carboxylic acid esters and the phosphoric acid esters is contained in the non-aqueous electrolyte. Especially preferably, at least one organic compound selected from the group consisting of the cyclic carboxylic acid esters and the phosphoric acid esters is contained in the non-aqueous electrolyte. This is because flash point and ignition point of these compounds are very high and, hence, batteries higher in safety can be obtained.

[0010]

As the electrolyte salts dissolved in these organic solvents, mention may be made of, for example, LiClO_4 , LiBF_4 , LiPF_6 , LiAlCl_4 , LiSbF_6 , LiSCN , LiCl , LiCF_3SO_3 , LiCF_3CO_2 , LiAsF_6 , $\text{LiB}_{10}\text{Cl}_{10}$, lithium salts of lower aliphatic carboxylic acids, LiCl , LiBr , LiI , chloroborane lithium, lithium tetraphenylborate, salts having an imide skeleton ($(\text{C}_2\text{F}_5\text{SO}_2)_2\text{NLi}$, $(\text{CF}_3\text{SO}_2)_2\text{NLi}$, $(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)\text{NLi}$, etc.), and salts having a methide skeleton ($(\text{CF}_3\text{SO}_2)_3\text{CLi}$, etc.). These may be used each alone or in combination of two or more in the electrolyte and the like, and LiPF_6 is especially preferred. Amount of the lithium salts dissolved in the non-aqueous solvent is not especially limited, but preferably is 0.2-2 mol/l, especially preferably 0.5-1.5 mol/l.

[0011]

Furthermore, in order to make the electrolyte nonflammable, halogen-containing solvents such as carbon tetrachloride and ethylene trifluoride chloride can be
5 contained in the electrolyte. Moreover, carbon dioxide can be contained in the electrolyte for giving suitability for high-temperature storage.

[0012]

Furthermore, there may be used a gel
10 electrolyte comprising an organic solid electrolyte which contains the above non-aqueous electrolyte. As the organic solid electrolyte, effective are polymeric matrix materials such as polyethylene oxide, polypropylene oxide, polyphosphazene, polyaziridine,
15 polyethylene sulfide, polyvinyl alcohol, polyvinylidene fluoride and polyhexafluoropropylene, and derivatives, mixtures and composite thereof. Especially preferred are copolymers of vinylidene fluoride and hexafluoropropylene and mixtures of polyvinylidene
20 fluoride and polyethylene oxide.

[0013]

The negative electrode materials used in the present invention may be compounds capable of occluding or discharging lithium ions, such as lithium, lithium
25 alloys, alloys, intermetallic compounds, carbon materials, organic compounds, inorganic compounds, metal complexes, and organic high molecular compounds. These may be used each alone or in combination.

[0014]

The effect of the present invention is especially high when the negative electrode materials are carbon materials. Examples of the carbonaceous materials are cokes, pyrolytic carbons, natural graphite, artificial graphite, mesocarbon microbeads, graphitized mesophase spherules, vapor deposited carbons, glassy carbons, carbon fibers (polyacrylonitrile fibers, pitch fibers, cellulose fibers and vapor deposited carbon fibers), amorphous carbons, and carbons prepared by firing organic materials. These may be used each alone or in combination. Among them, preferred are graphite materials such as those obtained by graphitizing mesophase spherules at high temperatures, natural graphite and artificial graphite. The content is preferably 0-10% by weight.

[0015]

As the positive electrode active materials, there may be used those which can be generally used for non-aqueous electrolyte batteries. Examples thereof are Li_xCoO_2 , Li_xNiO_2 , Li_xMnO_2 , and $\text{Li}_x\text{Mn}_2\text{O}_4$ ($0 < x \leq 1.2$).

[0016]

Examples

Examples of the present invention will be explained referring to the drawings.

[0017]

Example 1

FIG. 1 is a longitudinal sectional view of a cylindrical battery used in this example. In FIG. 1, 1 indicates a battery case made by working a stainless steel plate having resistance to organic electrolyte, 2 indicates a sealing plate provided with a safety valve, and 3 indicates an insulation packing. The numeral 4 indicates an electrode plate group, and a positive electrode and a negative electrode between which a separator is disposed are rolled a plurality of times into a spiral form and inserted in the case 1. A positive electrode lead 5 is drawn from the positive electrode and connected to the sealing plate 2, and a negative electrode lead 6 is drawn from the negative electrode and connected to the bottom of the battery case 1. The numeral 7 indicates an insulation ring, which is provided at the upper and lower portion of the electrode plate group 4. The positive electrode, the negative electrode, and others will be explained in detail below.

[0018]

As for the positive electrode, a positive electrode mix paste was prepared by mixing an LiCoO_2 powder synthesized by firing a mixture of Li_2CO_3 and Co_3O_4 at 900°C for 10 hours with 3% of acetylene black and 7% of a fluorocarbon resin binder based on the weight of the LiCoO_2 powder, and suspending the mixture in an aqueous carboxymethyl cellulose solution to prepare a paste. The resulting positive electrode mix paste was

coated on an aluminum foil of 30 μ m in thickness and dried, followed by rolling to make a positive electrode plate of 0.18 mm in thickness, 37 mm in width and 390 mm in length.

5 [0019]

For the negative electrode, mesophase spherules graphitized at a high temperature of 2800°C (hereinafter referred to as "mesophase graphite") was used. This mesophase graphite was mixed with 5% of a
10 styrene-butadiene rubber based on the weight of the mesophase graphite and then the mixture was suspended in an aqueous carboxymethyl cellulose solution to prepare a paste. This negative electrode mix paste was coated on both sides of a Cu foil of 0.02 mm in thickness and
15 dried, followed by rolling to make a negative electrode plate of 0.20 mm in thickness, 39 mm in width and 420 mm in length.

[0020]

An aluminum lead was attached to the positive
20 electrode plate and a nickel lead was attached to the negative electrode plate. A polypropylene separator of 0.025 mm in thickness, 45 mm in width and 950 mm in length disposed between the positive electrode plate and the negative electrode plate were rolled into a spiral
25 form and inserted in a battery case of 17.0 mm in diameter and 50.0 mm in height.

[0021]

The electrolyte used was one prepared by

dissolving 1 mol/liter of LiPF_6 in a solvent comprising a mixture of ethylene carbonate and diethyl carbonate at a volume ratio of 30:70, followed by adding thereto tris(2-carboxyethyl) isocyanurate in an amount of 0.2% by weight, 0.5% by weight or 1.0% by weight based on the electrolyte. The electrolyte was poured into the battery case, and then the case was sealed to make Batteries 1-3 of the present invention.

[0022]

10 Example 2

Cylindrical batteries of spiral type were made in the same manner as in Example 1, except that tris(2-methoxycarboxyethyl) isocyanurate was used in place of tris(2-carboxyethyl) isocyanurate. These were referred to as Batteries 4-6 of the present invention.

[0023]

Example 3

Cylindrical batteries of spiral type were made in the same manner as in Example 1, except that the electrolyte used was prepared by dissolving 1 mol/liter of LiPF_6 in γ -butyrolactone and adding thereto tris(2-carboxyethyl) isocyanurate in an amount of 0.2% by weight, 0.5% by weight or 1.0% by weight based on the electrolyte. The resulting batteries were referred to as Batteries 7-9 of the present invention.

[0024]

Example 4

Cylindrical batteries of spiral type were made

in the same manner as in Example 3, except that tris(2-methoxycarboxyethyl) isocyanurate was used in place of tris(2-carboxyethyl) isocyanurate. These batteries were referred to as Batteries 10-12 of the present invention.

5 [0025]

Example 5

Cylindrical batteries of spiral type were made in the same manner as in Example 1, except that the electrolyte used was prepared by dissolving 1 mol/liter
10 of LiPF_6 in trimethyl phosphate and adding thereto tris(2-carboxyethyl) isocyanurate in an amount of 0.2% by weight, 0.5% by weight or 1.0% by weight based on the electrolyte. These batteries were referred to as Batteries 13-15 of the present invention.

15 [0026]

Example 6

Cylindrical batteries of spiral type were made in the same manner as in Example 5, except that tris(2-methoxycarboxyethyl) isocyanurate was used in place of
20 tris(2-carboxyethyl) isocyanurate. These batteries were referred to as Batteries 16-18 of the present invention.

[0027]

Comparative Example 1

A cylindrical battery of spiral type was made
25 in the same manner as in Example 1, except that tris(2-carboxyethyl) isocyanurate was not added. This battery was referred to as comparative Battery 1.

[0028]

Comparative Example 2

A cylindrical battery of spiral type was made in the same manner as in Example 3, except that tris(2-carboxyethyl) isocyanurate was not added. This battery was referred to as comparative Battery 2.

[0029]

Comparative Example 3

A cylindrical battery of spiral type was made in the same manner as in Example 5, except that tris(2-carboxyethyl) isocyanurate was not added. This battery was referred to as comparative Battery 3.

[0030]

Then, five cells each of the Batteries 1-18 of the present invention and the comparative Batteries 1-3 were subjected to constant voltage charging at a limit current of 500 mA and a charging voltage of 4.2 V for a charging time of 2 hours at an environmental temperature of 20°C, and discharge characteristics of these batteries at 1A were examined in charging state. Then, these batteries in charging state were subjected to storage test at 80°C for 5 days, and the batteries after stored were also subjected to charging and discharging under the same conditions as above and capacity recovery rate after storage (capacity after storage/capacity before storage \times 100(%)) was obtained. The results are shown in Table 1.

[0031]

[Table 1]

	Electrolytes	Additives	Addition amount (wt%)	Capacity recovery rate after storage
Battery 1	1.0M LiPF ₆ EC/DEC (30/70) (vol%)	Tris(2-carboxyethyl)- isocyanurate	0.2	82.4%
Battery 2			0.5	89.8%
Battery 3			1.0	90.1%
Battery 4		Tris(2- methoxycarboxyethyl)- isocyanurate	0.2	83.3%
Battery 5			0.5	90.1%
Battery 6			1.0	90.3%
Comparative Battery 1	1.0M LiPF ₆ γ -Butyrolactone			66.5%
Battery 7		Tris(2-carboxyethyl)- isocyanurate	0.2	82.1%
Battery 8			0.5	83.5%
Battery 9			1.0	83.9%
Battery 10		Tris(2- methoxycarboxyethyl)- isocyanurate	0.2	85.7%
Battery 11			0.5	87.1%
Battery 12			1.0	87.9%
Comparative Battery 2	1.0M LiPF ₆ Trimethyl phosphate			45.3%
Battery 13		Tris(2-carboxyethyl)- isocyanurate	0.2	73.5%
Battery 14			0.5	77.9%
Battery 15			1.0	80.3%
Battery 16		Tris(2- methoxycarboxyethyl)- isocyanurate	0.2	77.3%
Battery 17			0.5	79.8%
Battery 18			1.0	81.2%
Comparative Battery 3				38.7%

[0032]

From Table 1, it can be seen that the capacity recovery rates after storage of Batteries 1-18 of the present invention were much superior to those of the comparative Batteries 1-3 to which the additives were not added, and thus the organic compounds added in the Examples were effective.

[0033]

Example 7

Furthermore, investigation was conducted on contents of the organic compounds, and the results are shown in FIG. 2. The batteries were made in the same manner as in Examples 1-6, except that the contents of the organic compounds were changed, and the tests were conducted in the same manner as above. As is clear from FIG. 2, an effect on capacity recovery rate after storage was already seen at 0.01% by weight. However, the discharge characteristics per se began to become inferior at 20% by weight. It is considered that this is because the electric conductivity of the electrolyte per se decreased. Thus, it is preferred that the content of the compound represented by the formula (3) is less than 20% by weight.

[0034]

[Effects of the Invention]

As explained above, according to the present invention, batteries excellent in storage characteristics and high in reliability can be provided

because at least one compound added forms a film on the surface of the negative electrode to prevent the electrolyte and the negative electrode from contacting with each other, and, thus, occurrence of decomposition
5 reaction of the electrolyte can be diminished.

[Brief Description of Drawings]

[FIG. 1]

A longitudinal sectional view of a cylindrical battery in the examples of the present invention and the
10 comparative examples.

[FIG. 2]

A graph which shows relations between amounts of the additives and capacity recovery rate.

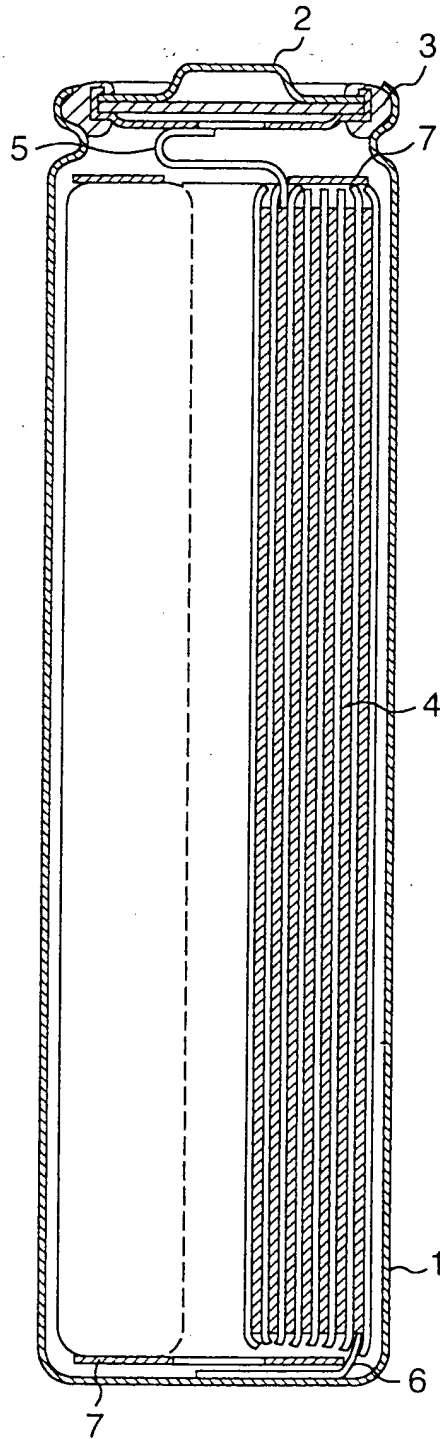
[Description of Reference Numerals]

- 1 Battery case
- 2 Sealing plate
- 3 Insulation packing
- 4 Electrode plate group
- 5 Positive electrode lead
- 6 Negative electrode lead
- 7 Insulation ring

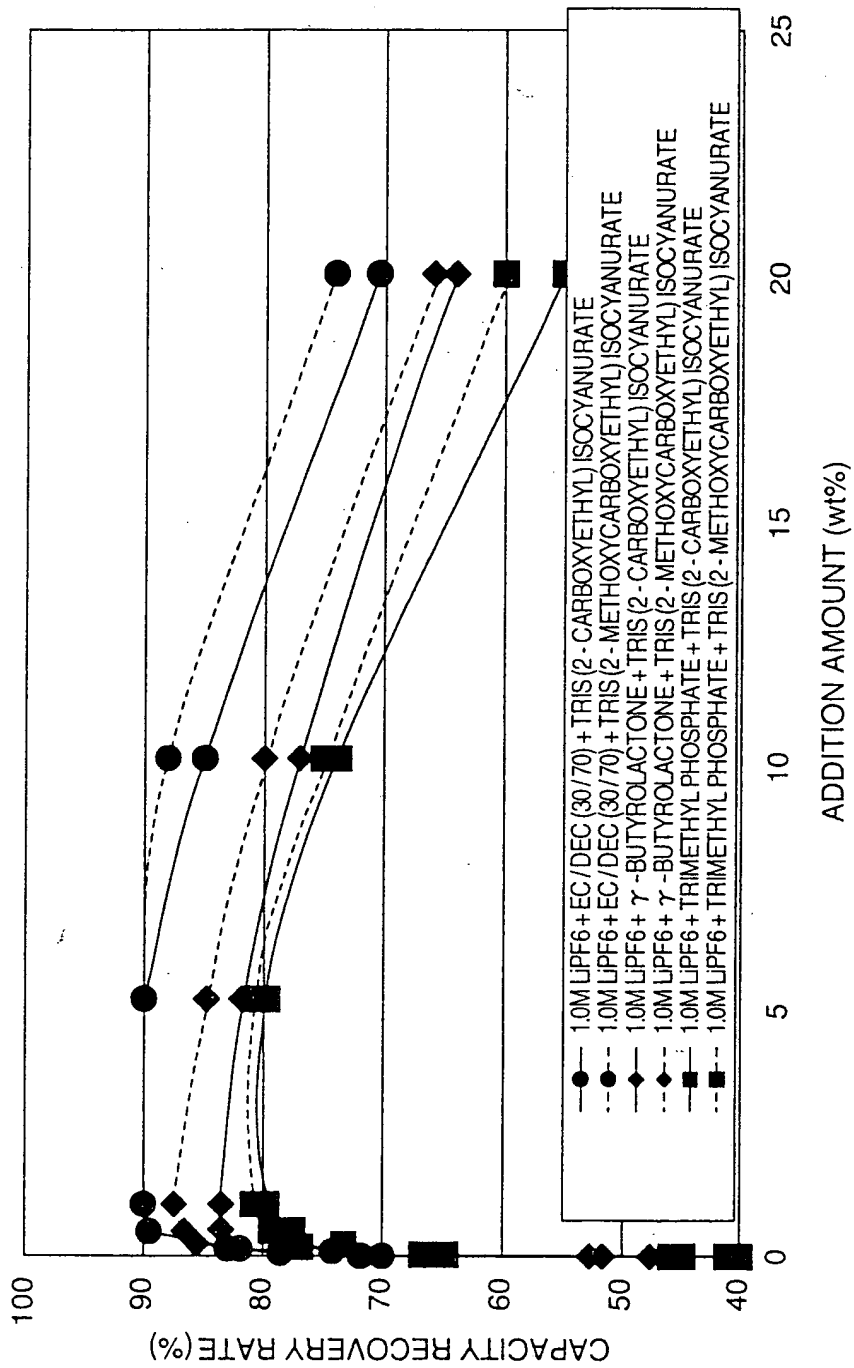
[Title of Document] Drawing

[Fig. 1]

FIG. 1



[Fig. 2]



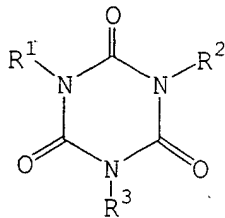
[Title of Document] Abstract

[Abstract]

[Problem] To provide a battery excellent in high temperature storage characteristics.

[Solving Means] A non-aqueous electrolyte battery excellent in high-temperature storage characteristics is provided by adding to the non-aqueous electrolyte a compound represented by the following formula:

[Formula 1]



(in the above formula, R¹, R² and R³ independently represent a hydrogen atom, a halogen atom or a straight chain or branched chain alkyl group).

[Selected Drawing] No